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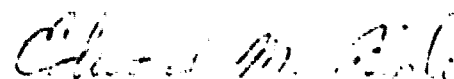
THE ORIGIN AND EVOLUTION OF SULFUR IN AN ARCHEAN  
VOLCANO-SEDIMENTARY BASIN - DEER LAKE AREA, MINNESOTA

By

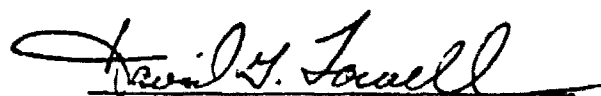
Dorian L. Nicol

Submitted to the faculty of the Graduate School  
in partial fulfillment of the requirements  
for the degree Master of Arts  
in the Department of Geology  
Indiana University  
May 1980

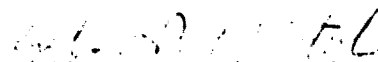
This thesis has been accepted as partial fulfillment of the requirements for the Master of Arts degree by the faculty of the Department of Geology, Indiana University.



Edward M. Ripley, Chairman



David G. Towell



Robert P. Wintsch

*Dedication*

*This work is dedicated to the memory of  
George L. Nicol - 'un hombre muy minero' -  
who taught me to follow the ore*

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### Acknowledgements

This project was funded by NASA grant NSG-7520 (Edward M. Ripley, principal investigator).

My thesis committee consisted of Edward M. Ripley, David G. Towell, and Robert P. Wintsch - to all of them go my sincere thanks for their advice, guidance, and patience.

My advisor, Ed Ripley, suggested this project to me and was helpful throughout all phases of its completion. He has served as a good advisor, teacher, and friend.

Dave Towell was very helpful in the interpretation stage of the project and in the final editing.

Bob Wintsch is perhaps the quintessential devil's advocate - he kept me honest.

David Meineke of the Minnesota Department of Natural Resources provided access to drill core stored in Hibbing, Minnesota.

Sally Corle helped me with sampling in Hibbing - I promised her an interesting job and she carried core boxes. Craig Moore listened to a lot of my ideas and helped me to identify the good ones. The list of other friends and colleagues who gave of their time and expertise in order to help me is too long to list in its entirety - they know I am grateful to them.

Drafting and photography were performed by the drafting staff of the Indiana State Geological Survey. Barbara Moore helped me with drafting during evenings and weekends, without pay.

The final manuscript was typed by Mrs. Thea Brown. For her sense of humor as well as for her typing ability, I am grateful.

Isotopic analyses were performed at the Pennsylvania State University, in the laboratory of Dr. Hiroshi Ohmoto. His students were helpful and patient in explaining operation of the mass spectrometer.

My old friend John Dickey provided moral and financial support when I decided to enter graduate school.

Finally, to the friends I have made among students, faculty, and staff in the Geology Department, Indiana University - thanks. They drank and danced with me when things went well, and were patient with my Greek temper when they didn't.



### Abstract

Rocks of the Deer Lake area, northcentral Minnesota, consist of Archean (age greater than 2.6 billion years) metasediments and metavolcanics intruded by mafic layered sills. Geologic and sulfur isotopic data suggest that sulfides in the sediments are bacteriogenic, having formed in response to the activity of sulfate reducing bacteria during diagenesis. Deposition of the sediments appears to have occurred in a deep marine basin with restricted circulation of seawater. The bulk of the sulfur in the igneous rocks is of deep-seated origin, but basal contacts of the sills show evidence of assimilation of biogenic sulfur from the intruded sediments. This assimilation of biogenic sulfur is the primary geochemical control of local Cu-Ni sulfide mineralization.

## Introduction

The purpose of this study is to understand the origin and evolution of sulfur in the Deer Lake Complex, an Archean (age greater than 2.6 b.y.) sequence of volcanic, sedimentary, and intrusive rocks in Northcentral Minnesota. Berkley (1972) defined the Deer Lake Complex as consisting of the intrusive rocks of the area, specifically the layered sills. In this study, the term Deer Lake Complex includes the whole suite of rocks in the Deer Lake area.

Specific objectives of this study are the following.

1. A determination of the role of sulfate-reducing bacteria in the genesis of pyrite found in the Deer Lake sediments.
2. A determination of the origin of sulfur in the igneous rocks, principally to determine whether sulfur in these rocks is of primary, magmatic origin, or due to assimilation or distillation of sulfur from the sedimentary country rocks.

Determination of the role of sulfate-reducing bacteria in producing sulfide incorporated into the sediments is of particular interest in light of recent efforts (for example, Monster et al, 1979) to bracket the time of appearance of these organisms.

Determination of the extent of sulfurization of the magma is interesting from an ore exploration viewpoint. The similarity of the geologic setting of the Deer Lake complex to that of Australian and Canadian massive and disseminated nickel and copper sulfide deposits (for example, Naldrett, 1973) spurred exploration by several mining companies in the early 1970's. After fairly extensive exploration, including diamond drilling, which had negative results except for the disclosure of small amounts of sulfide mineralization in the basal contacts of the intrusions, exploration was terminated.

Ripley (1973) has discussed geochemical characteristics of the Deer Lake Complex which rendered it unfavorable for the development of ore-grade mineralization, among them the low level of sulfur in the magmas. A major goal of this study is to determine whether or not the cause of the local pockets of mineralization was assimilation or distillation of sulfur from the intruded sediments. This is of interest in view of recent efforts (for example, Ripley, in press; Mainwaring and Naldrett, 1977) to assess the role of sulfurization of mafic and ultramafic magmas in producing magmatic Cu-Ni deposits.

## Geologic Setting

The Deer Lake area is located in the southern part of the Superior Province of the Canadian Shield, in Itasca County, Minnesota, approximately 100 miles northwest of Duluth (see Fig. 1). The study area includes sections 1, 2, 3, 10, 11, 12, 15, 16 and 17 of T.61N., R.25W. and sections 6 and 7 of T.62N., R.24W.

The Deer Lake Complex, composed of a lower Precambrian volcano-sedimentary sequence intruded by ultramafic and mafic sills, is surrounded by later Precambrian granitic plutons. Regional metamorphism is of lower greenschist facies. This lithologic association is typical of greenstone belts throughout the world (Anhaeusser et al, 1969).

Some 60 kilometers to the east of the Deer Lake Complex is the well-known Vermilion Belt, consisting of intercalated volcanics, graywackes, and slates intruded by ultramafic and mafic sills (Ojakangas, 1972; Sims, 1972). The lithological and structural resemblance of the Deer Lake area to the central and western portions of the Vermilion Belt lend support to the idea (Ripley, 1973) that the Deer Lake Complex is a faulted block of the Vermilion Belt.

The petrology and structural geology of the Deer Lake Complex have been well-described (Berkley, 1972; Ripley,

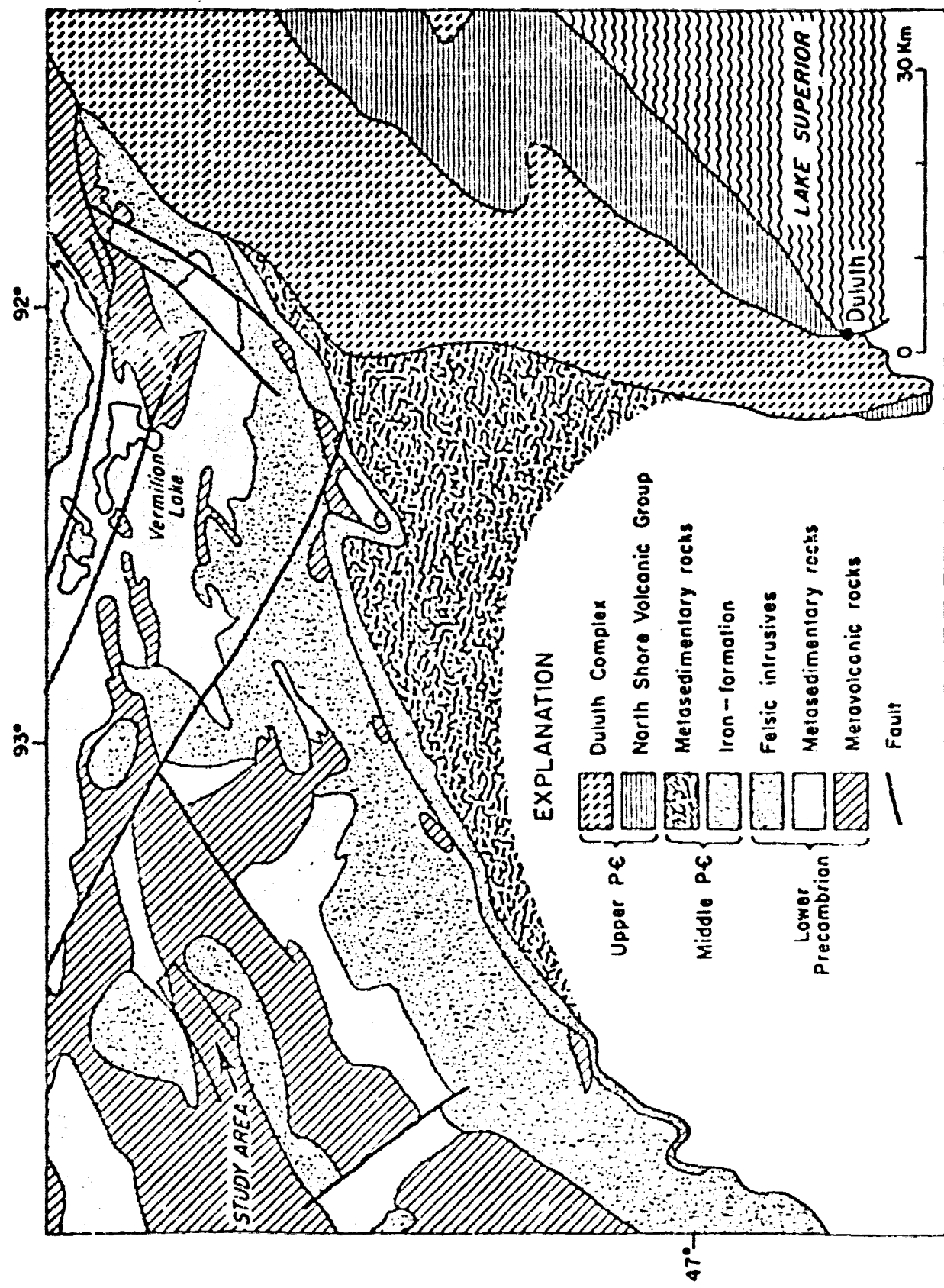
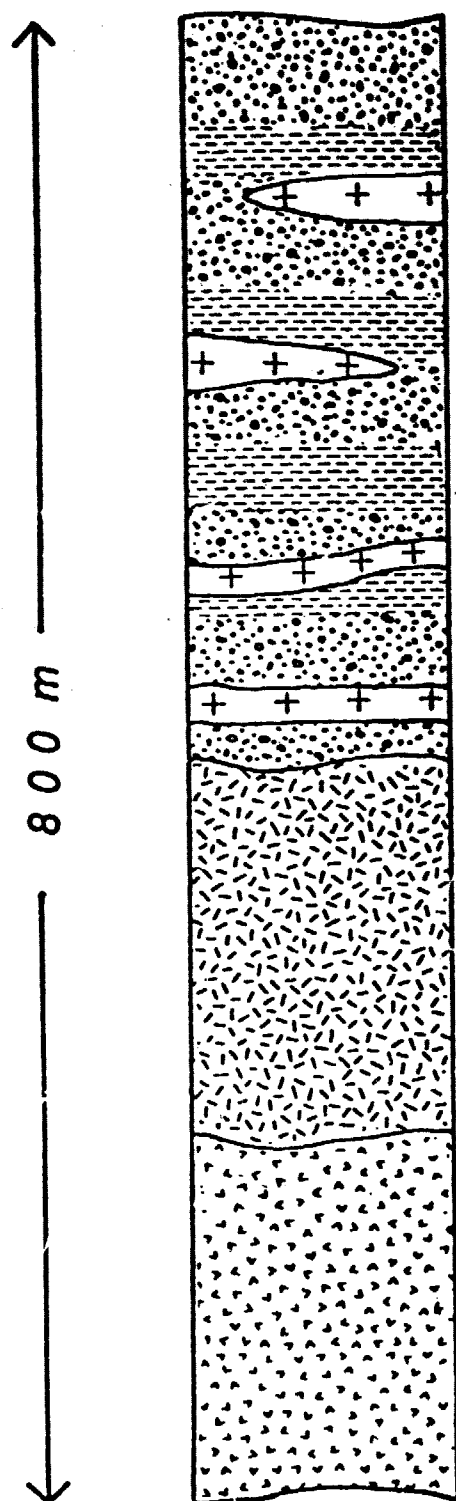


FIGURE 1.

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# Generalized Stratigraphy, Deer Lake Area, Itasca County, Minnesota



*Metagraywacke - slate  
sequence with  
intercalated basaltic  
flows*

*Layered peridotite -  
pyroxenite - gabbro  
sill 1*

*Layered peridotite -  
pyroxenite - gabbro  
sill 2*

Figure 2.

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1973, 1978; Berkley and Himmelberg, 1978) and are only briefly summarized here.

Figure 2 illustrates the general stratigraphy in a portion of the Deer Lake area. The oldest rocks in the area are those of the volcano-sedimentary sequence. Diabase dikes which crosscut the Deer Lake Complex have been assigned a K-Ar date of 2 billion years (Hanson and Malhotra, 1971), establishing a minimum age for these rocks. If the correlation of the Deer Lake rocks to those of the Vermilion District is accepted, then the 2.7 billion year old Soudan Iron Formation overlying the Vermilion District establishes 2.7 billion years as a minimum age.

The volcano-sedimentary rocks in Deer Lake can be divided into the following types:

1. Metavolcanics - These consist of pillowed metabasalts with a combined thickness of approximately 180 meters. Generally they underlie the sediments though locally sediments and volcanics are intercalated. They can be divided (Ripley, 1973) into at least eight individual flows.

2. Metagraywackes - These occur in distinct sequences never more than 10 meters thick and are thought to be derived at least partly from the underlying volcanics (Ripley, 1973).

Locally, the graywackes display graded bedding, but it is unclear whether or not they represent a turbidite sequence. The graywackes contain abundant disseminated pyrite (commonly up to 3%), occurring as distinct cubes, commonly 1-3 millimeters on a side.

3. Slates and Argillites - These occur as distinct sequences up to 15 meters in thickness, intercalated with the graywackes and volcanics, and are commonly black and carbonaceous. Their most striking feature is the abundance of large (up to 2 centimeters across) pyrite ovules.

The volcano-sedimentary sequence is intruded by a complex of igneous rocks comprised of two layered sills, a gabbroic body, and two ultramafic lenses. The sills are stacked and were emplaced stratigraphically below, and locally within, the volcanics. They are thought (Ripley 1973) to represent the lower portion of the volcanic system that produced the Deer Lake flows. Similar relationships between layered mafic sills and volcanic flows have been proposed by Irvine and Smith (1967), McCall (1973), and Upton and Wadsworth (1972) to account for the close spatial relation of sills and flows in Canada, Australia, and Réunion Island.

The sills have an average thickness each of 200 meters. Their layering consists of: a basal chilled zone overlain



successively by peridotite, pyroxenite, gabbro, locally a quartz diorite cap, and an upper chilled zone. The igneous petrology of these rocks is discussed in more detail in the aforementioned studies of Deer Lake geology.

Following emplacement of the sills, the Deer Lake area was subjected to three episodes of deformation during the early Precambrian and one during the middle Precambrian (Ripley, 1973). These events resulted in steep isoclinal folding and faulting characterized by dominance of either dip slip or strike slip movement.

The Deer Lake rocks are metamorphosed to lower green-schist facies. In general, metamorphism has preserved primary rock textures but altered mineralogies: the peridotites are extensively serpentized, pyroxenes have been altered to amphibole, and plagioclase has suffered saussuritic (chlorite, calcite, epidote, zoisite) alteration.

## Origin of Sulfides in the Sedimentary Rocks

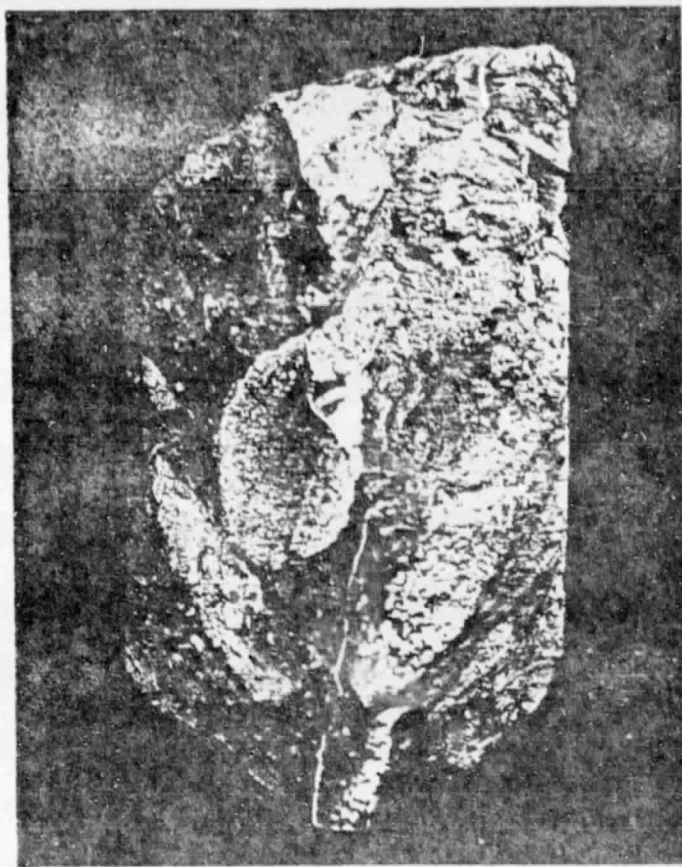
### Geology, Mineralogy, and Morphology of the Sulfide Mineralization

The black slates of the Deer Lake area are characterized by an abundance of pyrite ovules, some up to 2 centimeters in diameter (see Figure 3). On the basis of texture and appearance, the mineralization bears little if any resemblance to volcanogenic ore often associated with black slates (see, for example, Smirnov, 1976, or Garcia Palomero, 1977) which tend to display massive layers of essentially pure, fine-grained sulfides showing sedimentary structures (slump structures, graded bedding, etc.) and which have been interpreted as forming in response to the deposition of a sulfide-rich mud. Pyrite in the Deer Lake slates is confined to discreet ovules with no tendency toward massiveness and a complete lack of such sedimentary structure within each ovule.

The graywackes contain abundant (up to ~3%) disseminated pyrite. The pyrite occurs as discrete cubes, sometimes as large as several millimeters on a side, but more commonly one or two millimeters wide.

Sulfides in the sediments appear distributed quite homogeneously both vertically and horizontally. Locally, a concentration of sulfides (up to about 5%) along fractures is

a.



b.



Figure 3. a. pyrite ovules in slate  
b. ovules mounted on stubs for SEM

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noted. These are interpreted as remobilization of primary sulfide minerals. Generally, however, mineralization has little relationship to joint or fracture systems.

Pertinent to this discussion is the observation that with the exception of scattered, disseminated sulfide grains (less than 1%, mostly pyrrhotite), the volcanics that are intercalated with the sediments are essentially devoid of sulfide mineralization.

Standard polished sections of several pyrite ovules from the slates were prepared and examined under reflected light. The only sulfide mineral observed was pyrite, inevitably displaying a framboidal texture (Ramdohr, 1969).

Six ovules were removed from the slate with hydrofluoric acid following the methods of Neuerberg (1975 and 1961) and examined by scanning electron microscope. The pyrite maintains its framboidal morphology down to the smallest scale (see Figure 4). The significance of pyrite textures is discussed below.

Two questions arise regarding the origin of the pyrite in the Deer Lake sediments:

1. Nature of pyrite deposition - deposition by primary volcanic fluids or hydrothermal fluids (for example, circulating seawater) vs. diagenetic origin.

a.



b.

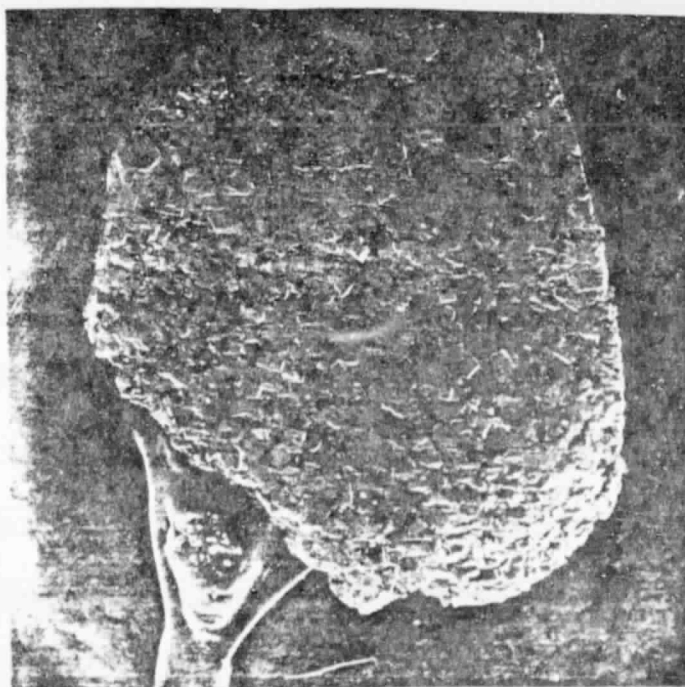


Figure 4. Scanning Electron Microphotographs of Pyrite Ovules  
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2. Origin of the sulfide in the pyrite - volcanic, biogenic, or a combination of the two.

Large (1977) has described chemical and geological characteristics of volcanogenic sulfide deposits. He divides volcanogenic deposits into two types:

1. Proximal - deposition directly overlying volcanic vents, associated with disseminated and vein mineralization in volcanic rocks.

2. Distal - deposition of sulfides as sediments in seafloor depressions away from the source vent.

Some deposits (for example, Rio Tinto, Spain) display both proximal and distal characteristics and allow one to trace the evolution of the volcanic ore fluid.

The absence of mineralization in the Deer Lake volcanics, and the lack of any massive sulfide accumulations, stockwork mineralization, or 'stringer' ore argue rather convincingly against a proximal volcanic origin of the pyrite in the Deer Lake sediments.

A distal volcanic origin, while considered unlikely, is more difficult to rule out. The restriction of mineralization to discreet ovules, and the absence of mineralized bands or massive sulfide accumulations, are strong, albeit not conclusive, arguments against a distal volcanic origin of the pyrite.

In summary, pyrite deposition by a primary volcanic fluid appears unlikely at Deer Lake. Alternative hypotheses of pyrite deposition as well as possible mechanisms of sulfide generation are discussed below in light of sulfur isotopic studies.

#### Sulfur Isotopic Data

Fifty samples of sulfide from Deer Lake sediments were prepared and analyzed for sulfur isotopic composition. The analyses were performed using a modified 6"60° sector Nuclide mass spectrometer at the Pennsylvania State University.

Larger sulfide grains were drilled mechanically and burned in a vacuum with an excess of CuO, yielding SO<sub>2</sub> for introduction into the mass spectrometer. Samples containing disseminated Sulfide were acid treated in a nitrogen atmosphere (Rye and Rye, 1974; Ripley, 1976). The resulting hydrogen sulfide was reacted with cadmium acetate to produce cadmium sulfide in turn reacted with silver nitrate to produce silver sulfide. The resulting silver sulfide was then burned with cupric oxide to yield sulfur dioxide for analysis.

The results of the isotopic analyses are expressed in terms of the  $\delta^{34}\text{S}$  notation, where

$$\delta^{34}\text{S} = \frac{\left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_{\text{sample}} - \left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_{\text{STD}}}{\left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_{\text{STD}}} \times 1000$$

the accepted standard being sulfur from the troilite phase of the Canyon Diablo meteorite, with  $^{34}\text{S}/^{32}\text{S} = .0450045$  (Hoefs, 1973). Sample reproducibility generally was within 0.3 o/oo.

$\delta^{34}\text{S}$  values for the Deer Lake sediments are presented in histogram form in Figure 5. Of interest are the range in observed values (-3 o/oo to +12 o/oo) and the peak at about +2 o/oo.  $\delta^{34}\text{S}$  values of the sediments vary widely over short distances (up to ~10 o/oo over a vertical distance of a few meters). This variation is erratic and does not follow any apparent stratigraphic or spatial trend.

Before proceeding with a discussion of the isotopic data regarding the origin of the sulfide minerals, a point can be made regarding the possible role of greenschist metamorphism in altering the sulfur isotopic ratios presently found in the sediments. Although metamorphism will alter the sulfur isotope distribution between coexisting sulfide minerals, the scale of redistribution is small and the overall sulfur isotopic composition of a horizon is preserved (for example, Ripley and Ohmoto, 1977; Rye and Ohmoto, 1974). Considering the low grade of Deer Lake metamorphism and the absence of sulfide phases in the sediments other than pyrite, the effect of metamorphism on the sulfur isotope ratios can be neglected.



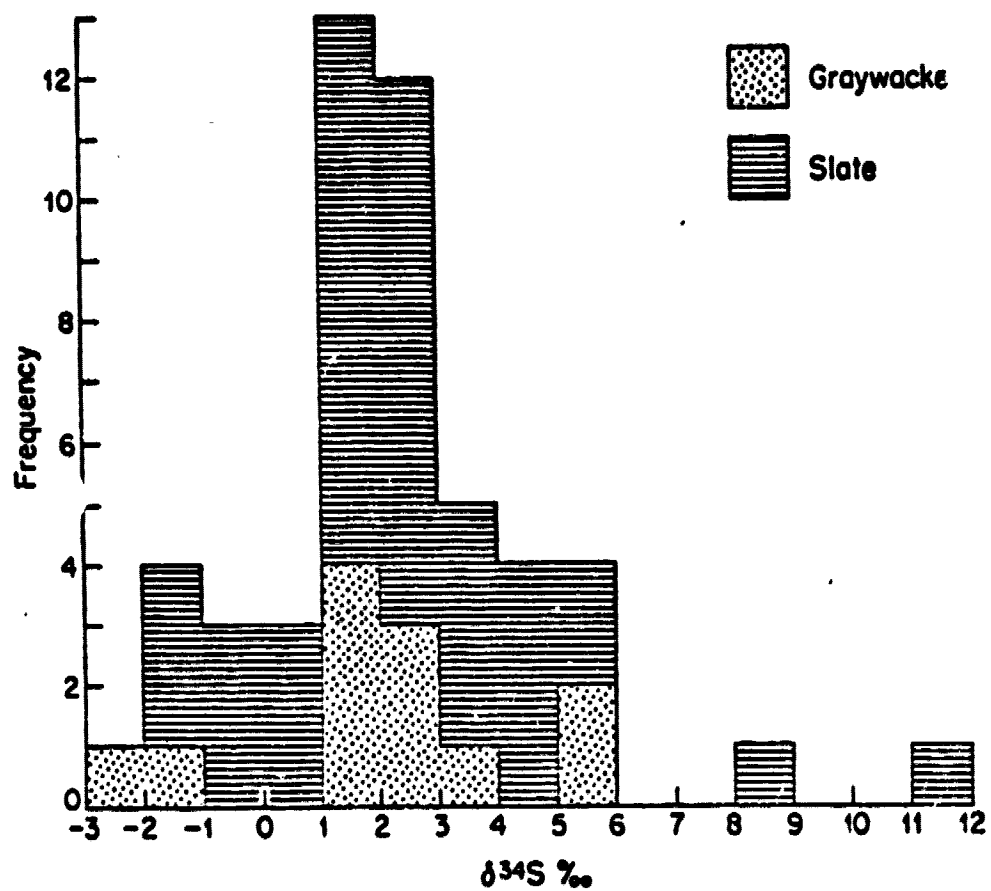


Figure 5. Sedimentary  $\delta^{34}\text{S}$  Values.

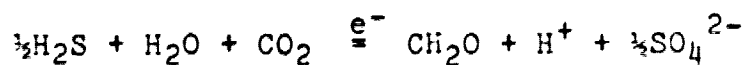
## Discussion

Having shown that pyrite deposition by igneous fluids is unlikely at Deer Lake, the possibility of their deposition being related to reduction of seawater sulfate suggests itself. Two mechanisms are possible:

1. Inorganic (nonbiogenic) reduction of seawater sulfate during circulation of seawater through the volcano-sedimentary pile.

2. Bacterial reduction of seawater sulfate during diagenesis of the sediments.

A crucial point is the question of the existence of sulfate in Archean seawater, preceding the onset (approximately 2 b.y. before present) of oxidizing weathering processes or the establishment of an atmospheric reservoir of free oxygen. The occurrence of barite in rocks of The Fig Tree Group, South Africa (Heinrichs and Reimer, 1977) indicates the likelihood of some amounts of sulfate being present in Archean seawater. Broda (1975) has proposed that green and purple sulfur oxidizing bacteria (photolithotrophic bacteria) supplied sulfate to seawater by reactions similar to:



Furthermore, some amounts of sulfate would have been available from volcanic activity. In other words, sulfate could have

become plentiful in the oceanic environment long before the attainment of free oxygen in the contemporaneous atmosphere.

Reduction of seawater sulfate could occur by both inorganic (not related to biological activity) and bacterial processes. These will be discussed separately and their possible role in the genesis of the pyrites evaluated in light of the geologic and isotopic evidence.

#### Inorganic Reduction of Seawater Sulfate

This hypothesis postulates a nonbiogenic reduction of seawater sulfate by material in the sediments, for example, methane, which could have been abundant in the Archean environment (Miller and Orgel, 1974), or ferrous iron contained in the volcanic rocks (possible at temperatures above about 250°C). Such a mechanism for deposition of the pyrite presupposes the following:

1. Heat associated with extrusion of the volcanics initiated a convective circulation of seawater through fractures in the volcano-sedimentary pile.
2. The sulfate contained in the circulating seawater was reduced by reaction with organic compounds such as methane

in the sediments (for example,  $\text{CH}_4 + 2\text{H}^+ + \text{SO}_4^{2-} = \text{CO}_2 + \text{H}_2\text{S} + 2\text{H}_2\text{O}$ ) or with ferrous iron contained in the volcanics (for example,  $8\text{Fe}^{2+} + \text{SO}_4^{2-} + 10\text{H}^+ = 8\text{Fe}^{3+} + \text{H}_2\text{S} + 4\text{H}_2\text{O}$ ).

3. The resulting sulfide reacted with available metal to precipitate as metal sulfide.

Mechanisms similar to this have been used with considerable success to explain various ore deposits throughout the world (see, for example, Ohmoto and Rye, 1974 and Ripley and Ohmoto, 1977).

Figure 6 illustrates the  $\delta^{34}\text{S}$  distributions one might expect from reduction of seawater sulfate. Note that inorganic reduction of seawater sulfate of a fixed  $\delta^{34}\text{S}$  has the potential to give rise to sulfides with widely varying values. Under certain conditions, small changes in environment (pH,  $f\text{O}_2$ , etc.) can cause variations of up to 40 o/oo in  $\delta^{34}\text{S}$  of the generated sulfide (Ohmoto, 1972).

Assuming a  $\delta^{34}\text{S}$  for Archean seawater sulfate of +10 to +30 o/oo (see Holser and Kaplan, 1966; Schwarcz and Burnie, 1973), it would be possible to obtain a spread in  $\delta^{34}\text{S}$  values of generated sulfide similar to that observed in the Deer Lake sediments by an inorganic reduction. However, considerations

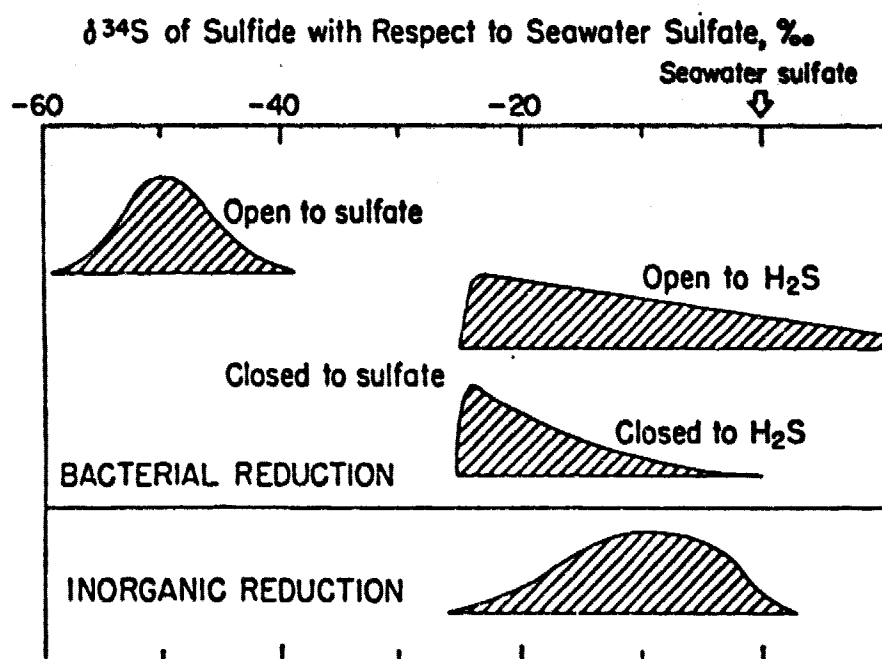


Figure 6. Predicted  $\delta^{34}\text{S}$  Values of Sulfide Generated from Seawater Sulfate (adapted from Ohmoto and Rye, 1979)

other than the isotopic data force this mechanism to be considered unlikely in the case of Deer Lake.

The style and field relationships of the sulfide mineralization are not consistent with an origin involving convective circulation of seawater. First, the restriction of abundant pyrite to the sediments argues against ore-fluid circulation through the volcano-sedimentary pile. The absence of other than traces of disseminated pyrite in the volcanics themselves certainly argues against a reduction of sulfate by ferrous iron in the volcanics.

Second, if deposition of the pyrite were due to circulating seawater, one would expect an abundance of mineralization along the fractures that served as pathways for the ore fluid. Other than some local mineralization along small fractures, no such association is seen. Indeed, the sulfides are distributed rather uniformly within the slates and graywackes, and do not appear to have any genetic relation with the volcanics. In summary, although an inorganic reduction of seawater sulfate cannot be completely ruled out as a source for the sulfide precipitating in the Deer Lake sediments, it must be considered an unlikely possibility.

## Bacterial Reduction of Seawater Sulfate

Bacteria similar to the species *Desulphovibrio desulphuricans* are known to reduce sulfate to sulfide. The following steps are involved in the reduction (Kemp and Thode, 1968):

1. Intake of sulfate
2. Organic complexing of sulfate
3. Reduction of sulfate to sulfite
4. Reduction of organically bound sulfite
5. Production of hydrogen sulfide

This bacterial reduction results in a kinetic isotopic fractionation effect, the resulting sulfide being enriched in  $^{32}\text{S}$ , hence "lighter", relative to the source sulfate. The isotopic composition of the produced hydrogen sulfide is very close to that of any resulting pyrite, the fractionation between hydrogen sulfide and pyrite being small at any temperature (Ohmoto, 1972).

The isotopic exchange between sulfate and sulfide may be described by considering the reactions



The kinetic isotope effect (Nakai and Jensen, 1960; Kemp and Thode, 1968) is defined as the ratio of the two rate constants

$k_{32}/k_{34}$ . At 25°C, the theoretical value of the kinetic fractionation for this reaction is 1.075 (Tudge and Thode, 1950). In other words, the hydrogen sulfide should be depleted in  $^{34}\text{S}$  by approximately 75 o/oo relative to the source sulfate. In fact, the actual value of this exchange constant can vary between rather wide limits depending on the following conditions:

1. Rate of the reduction - in turn dependent on such factors as temperature, pH, sulfate concentration, bacterial population density, etc.
2. Open vs. closed nature of the system (see Schwarcz and Burnie, 1973; Ohmoto and Rye, 1979). An open system is defined as one in which the rate of sulfate supply is faster than the rate of reduction (essentially, an infinite sulfate reservoir). A closed system is defined as one in which the rate of reduction is faster than the rate of sulfate supply (essentially, a limited sulfate reservoir).
3. If the system is closed, the extent to which the sulfate reservoir has been depleted.

Figure 6 shows the pyrite  $\delta^{34}\text{S}$  values one might expect from a bacterial reduction of seawater sulfate under conditions both open and closed to sulfate. Two cases are illustrated for the closed system - open to hydrogen sulfide (meaning that all the produced hydrogen sulfide reacted with ferrous iron to



precipitate as pyrite), and closed to hydrogen sulfide (meaning that only a fraction of the generated hydrogen sulfide precipitated as pyrite).

Schwarcz and Burnie (1973) have derived theoretical  $\delta^{34}\text{S}$  distribution curves similar to those shown in Figure 6. They demonstrate that open system bacterial reduction results in a fairly narrow spread of sulfide  $\delta^{34}\text{S}$  values approximately 40 to 60 ‰ lighter than the source sulfate. Closed system reduction, on the other hand, produces sulfides with values ranging from that of the source sulfate to  $\delta^{34}\text{S}$  of the source sulfate minus the maximum kinetic fractionation between sulfate and sulfide, with a peak located near the latter value.

The  $\delta^{34}\text{S}$  values of the Deer Lake sediments are most easily interpreted in terms of a closed system bacterial reduction. Such a reduction can be modeled by a Rayleigh distillation process (Faure, 1977). As the sulfide is enriched in  $^{32}\text{S}$ , the remaining sulfate reservoir becomes progressively enriched in  $^{34}\text{S}$ . This enrichment can be described by the Rayleigh equation:

$$\Delta = 1000 (f^{\alpha-1} - 1)$$

where

$$\Delta = (\delta^{34}\text{S}_{\text{SO}_4^{2-}})_{\text{instantaneous}} - (\delta^{34}\text{S}_{\text{SO}_4^{2-}})_{\text{original}}$$

$$f = \text{fraction of } \text{SO}_4^{2-} \text{ remaining}$$

and

$$\alpha = k_{34}/k_{32} .$$

It is difficult to assign values to the variables in this equation without knowing the isotopic composition of Archean seawater sulfate. Schwarcz and Burnie (1973) suggest that  $\delta^{34}\text{S}$  of seawater sulfate in the Archean did not vary outside the range +10 to +30 o/oo.

Rickard et al (1979) studied pyrite-barite deposits at Asen, Sweden (age: 1.8 b.y.) and concluded that their isotopic data ( $\delta^{34}\text{S}$  of pyrite: -14.8 to +8.4 o/oo) was consistent with a closed system bacterial reduction of a sulfate having  $\delta^{34}\text{S}$  of approximately +1 o/oo. They interpret the source sulfate as originating from local oxidation of volcanic sulfur ( $\delta^{34}\text{S}$  near 0 o/oo), which produces sulfate with  $\delta^{34}\text{S}$  near that of the original sulfide. Their model, well supported by their isotopic and geologic evidence, thus proposes the cycle sulfide to sulfate to sulfide.

The absence of highly negative values in the pyrites of the Deer Lake sediments argues against a similar situation obtaining at Deer Lake. If the source sulfate of the Deer Lake pyrites were at or near 0 o/oo, one would expect an abundance of pyrites with negative  $\delta^{34}\text{S}$  values, due to the kinetic fractionation effect. In light of estimates of the range in values of the kinetic effect (for example, Harrison and Thode, 1957; Nakai and Jensen, 1964), the range in  $\delta^{34}\text{S}$

values of the Deer Lake pyrites argues for a source sulfate no lighter than approximately +10 o/oo.

If, in fact, the Deer Lake sediments represent one of the earlier sites for the activity of sulfate reducing organisms, and such organisms had not been long present on earth at the time of deposition, then one can argue that seawater sulfate would not have been greatly enriched in  $^{34}\text{S}$  at the time of Deer Lake sedimentation, and accept as reasonable a value of +10 to +15 o/oo for  $\delta^{34}\text{S}$  of seawater sulfate. It must be admitted, however, that this is not strictly defensible, and does fall into the realm of speculation.

For the sake of example, a closed system bacterial reduction is modeled here using a value of +14 o/oo for the isotopic composition of source (seawater) sulfate. Use of a different source sulfate will alter the numbers, but the trends in this example will remain the same.

If we assume a value of +14 o/oo for seawater sulfate, then as a peak in  $\delta^{34}\text{S}$  values of the sulfides is located at about +2 o/oo, following the reasoning of Schwarcz and Burnie (1973),

$$(\delta^{34}\text{S}_{\text{SO}_4^{2-}} - \delta^{34}\text{S}_{\text{H}_2\text{S}})_{\text{max}} = -12 \text{ o/oo}$$

Then,  $\frac{K_{32}}{K_{34}} = 1.012$

and,  $\alpha = \frac{K_{34}}{K_{32}} = 0.988,$

which value lies within experimentally measured fractionations by sulfate reducing bacteria (for example, Harrison and Thode, 1957). The reduction is modeled as a function of extent of depletion of the sulfate reservoir in Table 1. Note that at about 50 percent reduction of sulfate to sulfide, there is a cutoff in observed  $\delta^{34}\text{S}$  values of pyrite. This is interpreted as indicating a limited abundance of metal; in other words, only the first 50 percent of produced sulfide was able to react with iron to precipitate as pyrite.

It must be emphasized that the Rayleigh model is presented here only as an illustration of principles. It does not quantitatively model the proposed reduction process. For example, the Rayleigh model would predict a trend toward heavier  $\delta^{34}\text{S}$  values as one moved upward stratigraphically. As the reduction proceeds, resulting sulfides are isotopically heavier than the preceding ones; these later sulfides would be located stratigraphically above the earlier ones. Such a trend is not apparent in the Deer Lake sediments. The inference is that the reduction process was more complicated than a simple, single batch process, and perhaps was affected by periodic influxes of fresh sulfate or occurred in several distinct batches.

Table I. Rayleigh model of closed system bacterial reduction

$$\text{Let } (\delta^{34}\text{S}_{\text{SO}_4^{2-}})_{\text{initial}} = +14 \text{ o/oo}$$

$$\text{Then } (\delta^{34}\text{S}_{\text{SO}_4^{2-}} - \delta^{34}\text{S}_{\text{H}_2\text{S}})_{\text{Max}} = -12$$

$$\text{And } \frac{k^{32}\text{S}}{k^{34}\text{S}} = 1.012; \alpha = \frac{k^{34}\text{S}}{k^{32}\text{S}} = 0.988$$

$$\text{Let } \Delta = (\delta^{34}\text{S}_{\text{SO}_4^{2-}})_{\text{instantaneous}} - (\delta^{34}\text{S}_{\text{SO}_4^{2-}})_{\text{initial}}$$

$f$  = fraction of  $\text{SO}_4^{2-}$  remaining

$$\text{Rayleigh Equation: } \Delta = 1000 (f^{\alpha-1} - 1)$$

$f$	$\Delta$ o/oo	$\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ o/oo	$\delta^{34}\text{S}_{\text{H}_2\text{S}}$ o/oo
1	0	14.00	2.00
.9	1.26	15.26	3.26
.8	2.68	16.68	4.68
.7	4.29	18.29	6.29
.6	6.15	20.15	8.15
.5	8.35	22.35	10.35
.4	11.06	25.06	cut-off in observed values

To summarize, the geologic and isotopic data are consistent with a diagenetic origin of the pyrite, with sulfide genesis due to bacterial reduction of seawater sulfate in a closed system of limited metal abundance. The resulting hydrogen sulfide reacted with ferrous iron during diagenesis to form the pyrite. It is easy to qualitatively model such a reduction process and see that it is consistent with the observed data, but impossible to model the process quantitatively without firm knowledge of the isotopic composition of seawater sulfate during the time of deposition of the Deer Lake sediments.

The framboidal morphology of the pyrite is not conclusive proof of a bacteriogenic origin (see, for example, Sweeney and Kaplan, 1973), but is consistent with it. Certainly, the morphology of the mineralization argues in favor of a syndepositional or diagenetic origin rather than an epigenetic origin. These observations support the hypothesis of bacterial reduction. Furthermore, the restriction of abundant pyrite to the sedimentary rocks argues favorably for the model involving bacterial reduction.

In conclusion, it is impossible on the basis of presently available data to unequivocally demonstrate a bacteriogenic origin for the pyrite of the Deer Lake sediments. However, a model of pyrite genesis involving bacterial reduction of

seawater sulfate fits the available geologic, mineralogical, and isotopic data better than any other mechanism. The data must be interpreted as strong, albeit not conclusive, evidence that sulfate reducing bacteria were operative during the time of deposition of the Deer Lake sediments.

#### Environment of Deposition

Closed system bacterial reduction has generally been interpreted (for example, Ohmoto and Rye, 1979, Schwarcz and Burnie, 1973) as indicating shallow, brackish water conditions. In the Deer Lake area, the presence of well developed pillow basalts and the sedimentary sequence shale - graywacke are clearly incompatible with shallow water conditions.

While one is reluctant to attempt to find modern analogues to Archean basins, present day marine basins with restricted circulation of seawater are well-known (see, for example, Gorsline, 1978), particularly along certain continental margins. A deep basin with restricted circulation of seawater would behave as a closed system in terms of bacterial reduction of seawater sulfate at or near the sediment - seawater interface. Furthermore, it must be considered that the reduction may occur below this interface and essentially be isolated from the seawater sulfate reservoir.

Slates and graywackes from the Onwatin Formation in Sudbury, Ontario (Thomson, 1956) have  $\delta^{34}\text{S}$  values somewhat similar to those of the Deer Lake sediments. Schwarcz and Burnie (1973) have proposed the existence of a deep marine basin with restricted seawater circulation to account for the apparent contradiction between lithologies indicative of deep water conditions and isotopic values indicative of closed system conditions.

To summarize, the rock types and sulfur isotopic data of the Deer Lake area suggest deposition in a deep, at least partly closed marine basin. Such basin conditions are known to exist today and are a reasonable geologic setting, though perhaps not for an area as small in serial extent as the Deer Lake area as it exists today. This again leads to speculation, as was discussed earlier, that at one time the Deer Lake Basin was part of the larger Vermilion Basin to the northeast. Such an interpretation is consistent with Sims' (1972) view of the regional geology and the relation between the greenstone belts of Northeastern Minnesota.

#### Implications

The evidence for the existence of sulfate reducing bacteria during deposition of the Deer Lake sediments is



particularly interesting in light of the recent study of Isua age (3.7 b.y. old) rocks from Greenland by Monster et al (1979). Monster and his coworkers found no evidence of the activity of sulfate - respirators in the Isua rocks.

Present thought on early stages of evolution (Peck, 1974 and Broda, 1975) supports the idea of photolithotrophic bacteria predating sulfate reducing bacteria. With the appearance of sulfate reducers prior to the appearance of an atmospheric reservoir of free oxygen, the sulfate reducers can be viewed as an important link in bioenergetic evolution from earlier forms of life, the green and purple bacteria, to the oxygen respirators.

In view of the conclusions of Monster et. al. (1979) that sulfate respirators were absent in Isuan time, their appearance can be dated as occurring between Isuan and Deer Lake times. Further efforts to bracket the time of their appearance must focus on this time interval.

### Origin of Sulfur in the Deer Lake Igneous Rocks

The distribution of sulfide minerals in the layered sills of the Deer Lake Complex has been well described by Ripley (1973, 1978) and is only briefly summarized here. Basal chilled zones of each sill contain locally abundant (up to 3 volume percent) sulfides, composed of pyrrhotite, cobaltian pentlandite, chalcopyrite, gersdorffite, and marcasite+pyrite (alteration products of pyrrhotite). The peridotites contain sparsely disseminated (up to 0.1 volume percent) pyrrhotite and pentlandite with minor chalcopyrite. Pyroxenites contain up to 0.25 volume percent sulfides, principally chalcopyrite and pyrrhotite. The gabbros contain pyrite and chalcopyrite with only occasional pyrrhotite, and the quartz diorite cap rock, where present, locally contains abundant pyrite. The stratigraphic distribution of sulfide minerals in the layered sills is easily understood in terms of an immiscible sulfide phase continuously separating from a silicate melt (see Ripley, 1979; Duke and Naldrett, 1978).

Ripley (1979) has shown that the Deer Lake magma was undersaturated with respect to sulfur, and has postulated assimilation of country rock sulfur along the basal contacts to explain the local mineralization.

### Sulfur Isotopic Data

Approximately thirty samples were prepared for analysis in the same way as were the sedimentary samples, and analyzed in the same mass spectrometer.

The results of these analyses are displayed in histogram form in Figure 7. Seven samples were analyzed in duplicate, with a reproducibility of approximately 0.2 o/oo.

### Discussion

The recognition of mixing of sedimentary sulfur with igneous sulfur ( $\delta^{34}\text{S}$  near 0 o/oo) is somewhat hindered in the Deer Lake area by the abundance of sedimentary sulfides themselves having a  $\delta^{34}\text{S}$  near 0 o/oo. However, the argument can be made that the sedimentary sulfur isotopic values are variable enough over short distances and contain enough heavy values that any substantial amount of contamination of igneous with sedimentary sulfur would be manifested by a trend toward heavier, positive values.

### Volcanic Rocks

$\delta^{34}\text{S}$  values of the volcanic rocks lie within the range -1 to +2 o/oo, with a peak at 0 to +1 o/oo. These values are interpreted as representing essentially pure juvenile sulfur, with

little or no mixing of sedimentary sulfur. The conclusion is that the magma which fed the Deer Lake volcanic system did not assimilate any considerable amount of sulfur from intruded sediments.

#### Intrusive Rocks

$\delta^{34}\text{S}$  values of rocks from the sills lie within the range -3 to +3 o/oo, with a peak in the range -1 to +1 o/oo.. These values also lie within the commonly accepted range for magmatic sulfur. The wider range in  $\delta^{34}\text{S}$  values may indicate some contamination by sedimentary sulfur, but the absence of  $\delta^{34}\text{S}$  values far removed from 0 and the undersaturation with respect to sulfur of the magma as a whole (Ripley, 1979) argue against any large scale contamination.

#### Chilled Zones

The relatively high positive  $\delta^{34}\text{S}$  values from some of the basal chilled zone material indicate substantial assimilation of sedimentary sulfur in the basal zones of the sills. The contamination is apparent over a vertical distance of approximately 5 meters. The  $\delta^{34}\text{S}$  values are heaviest at the base of the chilled zone and become lighter toward the top of the chilled zone, suggesting a model whereby isotopically heavy sedimentary sulfur is assimilated at the very base of the sill

and mixed with igneous sulfur, the ratio of igneous to sedimentary sulfur increasing as one moves stratigraphically upward in the sill.

In a recent paper, Ripley (1979) summarized chemical and petrologic data indicating that the concentration of sulfide minerals in the basal chilled zones was due to assimilation of country rock sulfur, but that the assimilation was not of great magnitude, and had only restricted, local effects on the magma. The sulfur isotopic data, as presented here, must be taken as supporting his conclusions, but raise a question as to the source of that sulfur. The values in the base of the chilled zone are higher than the bulk of values found in the Deer Lake sediments, suggesting that the contamination was due to local assimilation of sedimentary sulfur with a high  $\delta^{34}\text{S}$ , perhaps from a different sedimentary formation than those sampled in this study.

As the role of sulfurization of magmas in the genesis of certain ore deposits becomes more recognized (see, for example, Ripley, in press; Mainwaring and Naldrett, 1977), the question arises, what controls the extent to which assimilated sulfur is distributed through the magma? For example, evidence of sedimentary sulfur assimilation in the Duluth Complex persists well into the main body of an intrusion (Ripley, in press), while contamination effects in the Deer Lake Complex are much more spatially limited.

A thorough understanding of this question, and comparison of data from many different districts, will no doubt prove useful in future exploration for magmatic Cu-Ni deposits.

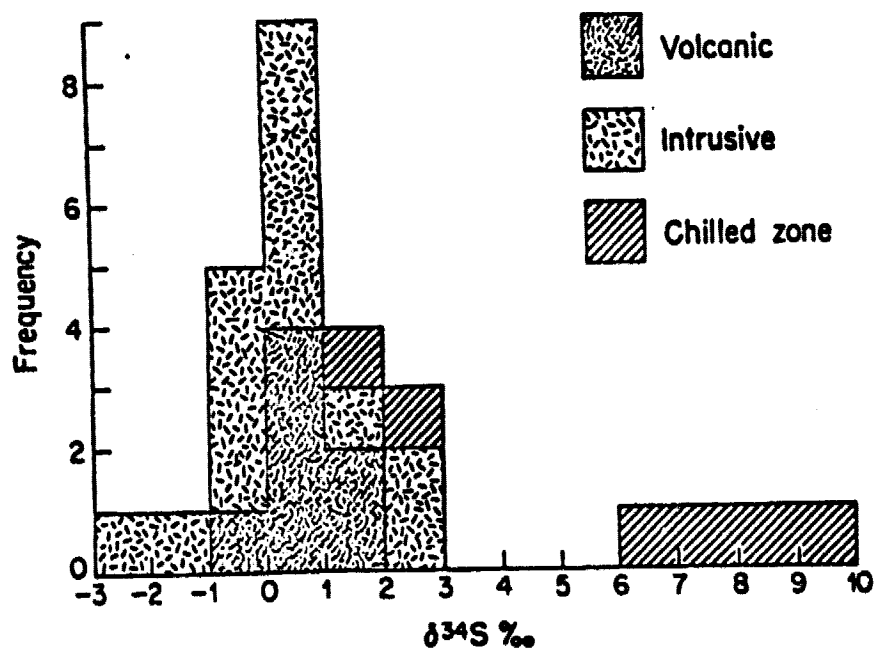


Figure 7. Igneous  $\delta^{34}\text{S}$  Values.

### Summary and Conclusions

1. Pyrite in the sedimentary rocks is biogenic in origin, having formed in response to the activity of sulfate-reducing bacteria.
2. The sediments were deposited in a deep marine basin with restricted circulation of seawater.
3. The igneous system as a whole was relatively sulfur-poor, as indicated by the low sulfide content.
4.  $\delta^{34}\text{S}$  values of the volcanics are all within the range -1 o/oo - +2 o/oo, indicating a deep-seated, juvenile source of sulfur.
5.  $\delta^{34}\text{S}$  values of the intrusions, exclusive of the chilled zones, range from -3 o/oo to +3 o/oo; this is within the accepted range of mantle-derived sulfur, but may represent some mixing with sedimentary sulfur.
6.  $\delta^{34}\text{S}$  values of the mineralized chilled zones indicate magmatic assimilation of sedimentary sulfur.
7. Local assimilation of sulfur by the magma was the cause of the local mineralization.



## Appendix I

This appendix gives a more detailed description of sample preparation and analytical techniques than was given in the text.

Polished sections were prepared in the Sample Preparation Laboratory of Indiana University (Ms. Cheryl Metz, Director).

Scanning Electron Microscope samples were prepared by dissolving the slate samples in hydrofluoric acid following the method of Neuerberg (1961 and 1975), leaving clean pyrite ovules. These were mounted on stubs with household cement and coated with gold - palladium alloy for viewing in the SEM.

Sulfides for isotopic analysis were extracted from samples by both mechanical and chemical means.

Larger sulfide grains were drilled using a dental - type drill, the resulting flakes of sulfide then being ground to powder in an agate mortar.

Figure 8 illustrates the sequence of chemical treatments used to extract sulfur from samples with disseminated sulfides. After boiling in the 1:1 hydrochloric acid the residual liquid was decanted and tested for aqueous sulfate. If sulfate was found to be present, the liquid was boiled again with a reducing acid solution (Thode Solution) composed of:

500 ml hydriodic acid

816 ml hydrochloric acid

245 ml hypophosphorous acid,

allowing for total extraction of sulfur from the sample.

After obtaining 20 to 60 milligrams of powdered sulfide, the powder was mixed with a stoichiometric excess of cupric oxide and burned in a vacuum at approximately 850°C to generate sulfur dioxide. The sulfur dioxide was separated from other reaction products (noncondensibles and carbon dioxide) by means of cryogenic traps.

The sulfur dioxide line was calibrated so that the percentage of sulfur dioxide yield for a given weight of burned sulfide could be estimated. Samples yielding less than approximately 80% of expected sulfur dioxide were either discarded or reburned and run in duplicate.

Several samples were prepared by both mechanical and chemical extraction of sulfur and run in duplicate. Sample reproducibility in these cases was within approximately 0.4 permil.

## Sample Preparation for Combustion

Sulfide-Bearing  
Sample  
(Approx. 1.0 gm)

+ 1:1 HCl; Thode Solution

+  $H_2S$  +  $N_2$  Stream

Absorbed in a Solution  
Containing Cadmium-Acetate (IN)

↓

Converted to Cadmium Sulfide  
(can not be easily filtered)

↓

Treated with .1 N  $AgNO_3$

↓

Silver Sulfide ( $Ag_2S$ )

↓

Heated until Coagulation

↓

Filtered

↓

Dried at  $100^{\circ}C$

Figure 8.

## Appendix II

Samples used in this study were obtained from drill core from diamond drill holes drilled by U. S. Steel Corporation during their minerals exploration program in the Deer Lake area. This core is currently in the possession of the Minnesota Department of Natural Resources, Hibbing, Minnesota.

The accompanying tabulation lists drill hole location and number, footage, lithology, and  $\delta^{34}\text{S}$  of each sample used in this study.

Drill Hole: 26502

Location: Sec. 12 T61N R25W

footage sampled	lithology	$\delta^{34}\text{S}$ o/oo
420.5	slate	1.55
421	slate	1.30
500	slate	1.07
501.5	slate	2.66
502	slate	3.34
503	slate	3.56
503.5	slate	1.75
504	slate	4.74
504.5	slate	2.87
505	slate	2.64
519.5	slate	3.11
520	slate	2.89
521	slate	2.87
522	slate	2.65
523	slate	3.32
650	volcanic	.26
705	volcanic	.49
866	gabbro	-.49
993	gabbro	2.26

## Drill Hole: 26503

Location: Sec. 12 T61N R25W

footage sampled	lithology	$\delta^{34}\text{S}$ o/oo
743	gabbro	.5
902	gabbro	.9
923.5	slate	1.09
986	volcanic	.97
988	slate	1.18
989	slate	-1.39
989.5	slate	.26
991	slate	-.52
991.5	slate	-.27
1025	slate	.31
1028	graywacke	1.36
1033.5	graywacke	3.68
1034	slate	.85
1037	slate	-1.41
1040	slate	-1.32
1140	graywacke	1.75
1141	slate	-.50
1142	graywacke	1.75
1143	graywacke	-1.39
1144	volcanic	.67
1145	volcanic	-.28
1146	volcanic	1.59

## Drill Hole: 26506

Location: Sec. 12 T61N R25W

footage sampled	lithology	$\delta^{34}\text{S}$ o/oo
270	gabbro	-2.59
319	slate	2.66
322	slate	1.76
327	slate	2.69
352.5	graywacke	1.75
404.5	graywacke	5.07

Drill Hole: 26508

Location: Sec. 12 T61N R25W

footage sampled	lithology	$\delta^{34}\text{S}$ o/oo
338	contact zone	9.02
401	slate	2.43
401.5	graywacke	2.99
436.5	volcanic	1.83
450	graywacke	2.65
464	graywacke	2.88
467	slate	1.75
483	slate	1.07
862.5	gabbro	1.83
893	gabbro	2.29
895	gabbro	-0.49

Drill Hole: 26509

Location: Sec. 10 T10N R25W

footage sampled	lithology	$\delta^{34}\text{S}$ o/oo
478	gabbro	0.9

Drill Hole: 26512

Location: Sec. 10 T61N R25W

footage sampled	lithology	$\delta^{34}\text{S}$ o/oo
808.5	gabbro	0.20
834.5	gabbro	0.26
836	gabbro	-1.64
839	gabbro	-0.49
853.5	gabbro	-0.82

## Drill Hole: 26515

Location: Sec. 16 T61N R25W

footage sampled	lithology	$\delta^{34}\text{S}$ o/oo
393	graywacke	+5.99
394	slate	4.43
395	slate	8.04
422	slate	4.33
422.5	slate	5.28
423	slate	4.65
423.5	slate	5.17

## Drill Hole: 26516

Location: Sec. 6 T61N R24W

footage sampled	lithology	$\delta^{34}\text{S}$ o/oo
329.5	slate	1.52
416	graywacke	-2.35

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